

DISBURSEMENTS

Inventors: **Richard C. Becker**, Ipswich, Massachusetts
Stephen L. Bunker, Wakefield, Massachusetts

1

FIELD OF INVENTION

Q17

The present invention relates to a method for producing boron-rich coatings for a variety of uses related to surface protection, sputter targets, electrically conductive layers, semiconductor compatibility, neutron absorption, high temperature bonding, and reactive chemistry.

BACKGROUND OF INVENTION

09560518-042800

Elemental boron is a well-known hard, covalent material. It also possesses considerable chemical resistance and is suitable for high temperatures in a vacuum or reducing atmosphere. It is known to impart considerable wear resistance to tooling materials if the boron can be added in sufficient quantity or coated on the workpieces. Unfortunately, elemental boron is difficult to deposit at a high rate by most commonly used deposition techniques, such as flame spray, plasma spray, or cathodic arc, because as a covalent material, it does not readily conduct electricity (resistivity $\sim 10^{14}$ microhm-cm).

Many boride compounds do conduct electricity very well. For example, metal boride compounds, such as TiB_2 , VB_2 , CrB_2 , and LaB_6 have electrical resistivity in the range of 5 to 20 microhm-cm. However, these common boron compounds typically contain boron at a concentration only between 50 and 86 atomic %, and their use in a deposition process, such as plasma spray, would result in a coating containing a high concentration of the metal (14 to 50 atomic percent). It is possible to avoid the electrical conductivity problem by making use of the unusual properties of a novel class of metal boride compounds which typically consist of a

SECRET

SECRET

[illegible]

represents the element include, but are not necessarily limited to, Dy, Er, Eu, Gd, Ho, Lu, Np, Pa, Pu, Sm, Tb, Th, Tm, Y, and Yb. All of these latter elements are only in group 3A of the periodic table, which includes the rare earths, the lanthanides and the actinides. There have also been reported three other compounds with unusual boron-to-element atomic ratios, $B_{25}N$, NaB_{15} , NaB_{16} , and YbB_{100} . While most elements of the periodic table are known to make borides, only these elements produce highly boron-rich borides. There is also considerable overlap between the boride lists for 12 and 66 boron atoms. There are also a few examples of MB_{12} in group 1A, group 2A, group 3A, group 3B, group 5A and group 6A of the periodic table. The only reported example in groups 4B, 5B, or 6B is ZrB_{12} .

The use of group designations used here is based on common American usage. The earlier nomenclature would be group 1B instead of 1A for the first column of the periodic table. The column containing yttrium and the rare earth elements is now 3B but used to be 3A. The IUPAC recommends that this column be designated 3, but this is not yet universally accepted.

Examples of the group in which the boron evaporates at a lower temperature compared to the companion element include the borides of yttrium, gadolinium, terbium, holmium, erbium, thulium, and lutetium.

In addition to the known examples of boron-rich boride compounds, it is also possible to dope boron with small amounts of elements that can affect the electrical conductivity. Doping is the dissolution of the element in the boron crystal, and unlike compound formation, does not require a specific stoichiometric ratio between the element and the boron. This is an alternative method for producing an electrically conducting boron material which consists substantially of the element boron. An impure sample of a boron-rich boride in which the stoichiometric ratio of

the elements is somewhat different from that of a known compound may consist of a mixture of a known compound and doped boron material.

The known applications for inexpensive, easily deposited thick boron coatings are numerous. The general applications include, but are not limited to, those stated in the following list.

- 1) Electrically conducting coatings on electrical insulators and ceramics.

Using the method of plasma spray, boron-rich borides can be deposited onto a wide variety of ceramics and insulators including BN, Al_2O_3 , aerogel, ZrO_2 , quartz, and porcelain. Adhesion of borides to these materials, as well as to most metals, carbon, carbides, and nitrides is particularly strong. No substrate material has been encountered in which the plasma sprayed yttrium boride did not stick tightly to the surface, as long as the substrate is not thermally damaged by the deposition process.

- 2) Interior surfaces of semiconductor fabrication machines to minimize evolution of impurities.

Semiconductor wafers are particularly sensitive to impurity particles, such as metal dusts, that are deposited on wafers during a vacuum fabrication process. In order to avoid this phenomenon many semiconductor fabrication machines are now coated with silicon (not an impurity) on their interiors. The silicon is expensive to deposit over large areas and does not conduct electricity well, a problem leading to static charging of surfaces in processing equipment that employs charged particles. A thick conductive boron coating would avoid this problem, since boron is a natural dopant for silicon.

- 003240" 81505560
- 3) Boron-coated refractory hot filaments, such as tungsten, tantalum, or rhenium, to enhance electron output and minimize emission of metal vapor in high purity processing situations. See for example, US patent 3,631,291 by Louis J Favreau which utilizes a conductive coating of LaB_6 , which patent is incorporated herein by reference.

In some processing applications, particularly those for semiconductors, surface contamination from tungsten or tantalum impurities emitted from a nearby heated filament due to evaporation or sputtering is undesirable. A conductive boron-rich boride can be coated on such filaments using a method such as plasma spray. The resultant boron-rich coating readily emits electrons and substantially only boron vapor if the coating boride is selected from the group in which boron evaporates more readily than the metal. Since the coating is producing the electron emission, it is not necessary for the hot filament substrate to be a good electron emitting material. Other refractory materials, such as carbon, carbides, or nitrides, could be employed.

Coating technologies, such as plasma spray, can also produce free-standing filaments and heating elements without the requirement of a permanently attached substrate. The coating is built up into a mold, and when sufficient thickness is obtained, a mold release allows the removal of an independent, free-standing structure. This method permits the fabrication of a substantially pure boron filament without any contaminating substrate material.

- 4) Chemically resistant surface coating on containers.

Borides are well known to be highly resistant to many forms of chemical attack, particularly those due to high temperature molten metals, as long as a vacuum or reducing environment is maintained. Such chemically resistant surface coatings can be fabricated using a variety of well-known deposition techniques, such as salt bath, powder coating, chemical vapor

deposition, and evaporation. See, for example, US patent 4,536,224 by Beyer et al. for salt bath, US patent 5,441,762 by Paul E. Gray et al. for coating with boride powder combined with chemical vapor deposition, US patent 3,985,917 by Val J. Krukoni for chemical vapor deposition, and JP 10,068,069A by Satoru et al. for evaporation, each of which patents are each incorporated herein by reference. Electrically conductive boron-rich boride permits the use of a much broader selection of deposition methods which can be less expensive or more suitable for large area surface coating of such reaction crucibles and related apparatus.

Similar to the application example of refractory hot filaments, it is also possible to make a free-standing container of substantially pure boron by plasma spray coating a mold or mandril and subsequently separating the thick coating from the mold or mandril substrate.

Satoru et al. describe electric arc evaporative coating of borides in which the metal component of the boride is selected solely from Groups 4B, 5B, and 6B of the periodic table. Satoru et al. do not teach the advantages of selecting the ultra-high atomic percent borides that are found solely in Group 3B together with the rare earth elements for their application.

- 5) Wear and corrosion resistant coatings for tooling. See for example, US patent 4,192,983 by Alfred J. Paoletti, incorporated herein by reference.

Boride coatings are known for their extreme hardness. Coatings can be applied to tooling by any of several techniques, such as plasma spray, and as stated in example 1) above, adhesion is sufficient to permit grinding and polishing into shape if required. It has also been demonstrated that in the presence of a diffusable layer of boron-rich boride, adhesion of materials as dissimilar as tantalum and graphite may be promoted. This property is of great significance for bonding tools to toolstocks and general refractory bonding technology.

possible to combine a well-known neutron absorbing element with boron in a suitable boride. See for example, US patent 5,273,709 by Danny C. Halverson et al., which is based on Gd combined with B₄C. Halverson et al. do not teach the advantages of selecting the ultra-high atomic percent borides that are found solely in Group 3B together with the rare earth elements for their application. These patents are also incorporated herein by reference.

- 8) Source for emission of clusters of boron atoms useful in space propulsion thrusters or ion sources.

Ion thrusters are currently used in space propulsion. Boron₁₂ ion clusters are the most common cluster species in the generated plasma. It has approximately the same mass as xenon, which is the heaviest noble gas available, and provides the greatest thrust. Being an electrically conductive solid state material, storage problems are eliminated, and potential energy per stored unit volume ratios increase significantly. Proper design engineering has demonstrated that after stable ignition has been established, the carrier gas may be eliminated and a self-sustaining discharge maintained.

- 9) Surface and/or bulk modification of metals, ceramics, and matrix materials.

The generated boron vapor may be introduced during fabrication, processing, and/or post-processing to modify properties of resultant materials. For example vapor or vaporizable material may be introduced into molten steel or other material at some state during the production process for purposes of altering hardness, chemical resistance, electrical properties, temperature resistance, etc. Boron is currently used in many of these areas. The novel properties of these boron-rich materials offer many valuable possibilities.

10) Protective coatings for fibers:

A common application is to coat the reinforcement fibers of composite materials with a boride compound in order to chemically protect the fiber from the corrosive molten binder material. See for example US patent 5,354,615 by Tenhover et al., incorporated herein by reference. Tenhover teaches the use of boride coatings of Y, Sc, Gd, Tb, Dy, Ho, and Er of the chemical form R_xB_{1-x} , where x is from about 0.05 to about 0.66. This range of x is equivalent to a boron-to-metal atomic ratio of 19 to 0.5. Tenhover et al. do not teach the advantages of ultra-high boron-to metal atomic ratios in excess of 19, which produce a more boron-like coating than is possible with lower ratios.

11) Erosion-resistant coating

Boron and boride coatings are usually extremely hard. They have demonstrated usefulness for reducing the surface erosion caused by macro-particle bombardment. See for example, US Patent # JP10148102A by Ikeda Kazuaki and Fujiwara Toshihiro, "Turbine Nozzle and Boride Covering Method Therefor", 1998, incorporated herein by reference. Examples of applications include compressor and turbine blades, steam generator components, and slurry-handling devices.

Boron or borides have been successfully coated onto substrates by a variety of well known methods. The most commonly described coating techniques are thermally induced evaporation of the element or of various borides, thermal diffusion of boron atoms into a surface, sputtering of any of the common electrically conductive borides with a boron-to-metal ratio less than 12, chemical vapor deposition, and molten salt bath. Other techniques described involve a

mixture of these techniques, such as the cementing of boron or boride powder to a surface using a chemical binder combined with either chemical vapor deposition or thermal diffusion.

While these coating methods are compatible with the deposition of boron coatings, there exist a number of other commonly employed industrial coating techniques which offer various advantages in coating rate, ultimate coating thickness, or ultimate coating density. Magnetron DC sputtering of elemental boron is considered difficult, because the element is not electrically conductive and thus requires the far more inefficient method of RF or pulsed sputtering to frequently discharge the sputtering target. Similarly, plasma spray of elemental boron has been attempted on numerous occasions, but the high thermal stability of boron combined with the lack of electrical conductivity make the plasma stream very difficult to maintain and thus not commercially practical. Cathodic arc is another of the high throwing power industrial coating methods that does not perform well with elemental boron. Cathodic arc depends on making the feedstock of elemental boron the cathode of an anode-cathode arc discharge, and this requires electrical conductivity of the boron.

The methods of depositing boron may also be combined with the deposition of other coatings simultaneously as well as with the co-bombardment of energetic ions for enhancing the final density of the coating. Many other well-known combinations of deposition techniques exist which are compatible with the methods of depositing boron described herein.

Given that the boron precursor compound is electrically conductive, the following well known methods may be employed to deposit the coating. The advantage is that no special modification of the standard deposition technique is required to accommodate the electrically conductive boride.

[illegible]

2) Cathodic arc:

12

003240-87509560
09560518-042800

sintered boride cathode target, a melted boride powder, or a thick boride coating deposited onto a graphite or metal substrate by a technique such as plasma spray. Cathodic arc is defined here to encompass a wide variety of processes that utilize electric arc heating of a solid over sufficiently small areas to produce sufficient local heating to both vaporize the solid and cause the thermionic emission of large quantities of electrons. The resulting mixture of partially ionized vapor and uncharged particles impinges on a workpiece where a coating forms. The process may optionally include a selection of a carrier gas species and its ambient pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

3) Cathodic arc with mass filter:

This technique is useful for producing a high current of boron ions. Such a high current can be accelerated and impinged onto a workpiece. Such implanted ions may also be thermally diffused for boridizing the workpiece if the workpiece is maintained or post-processed at a sufficiently high temperature. Mass filtered cathodic arc is defined here to encompass a cathodic arc source combined with the addition of electric fields, magnetic fields, or both types of fields between the cathodic arc source and the workpiece such that the uncharged particulate or gas vapor material from the cathodic arc source is preferentially and substantially eliminated in the flux being transferred to form the coating. The process may optionally include a selection of a carrier gas species and its ambient pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during

material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as ion boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

4) Sputtering:

Elemental boron can be slowly sputtered using RF sputtering methods because it is an electrical insulator. However, the electrically conducting boride can be readily sputtered by the more efficient D.C. magnetron sputtering process or ion beam bombardment sputtering. Sputtering is defined here to encompass the class of coating processes that utilize ion bombardment of a source of material in order to dislodge and transfer individual atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. The many variations of this process have a wide variety of specialized names including, but not limited to, D.C. magnetron sputtering, R.F. magnetron sputtering, AC magnetron sputtering, ion beam sputtering, D.C. sputtering, RF sputtering, or pulsed sputtering. The process may optionally include a selection of an ambient gas species and its ambient pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

5) Electric arc evaporation:

While elemental boron can be evaporated using electron beam or thermal boat evaporation methods, it is also possible to rapidly evaporate the metal boride using the heating

produced as electric current flows through the solid boride. Electric arc is defined here to encompass the class of evaporative coating processes that utilize an electric arc discharge between anode and cathode electrodes in order to heat and vaporize either the anode or cathode or both as a source of material in order to transfer individual atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. Electrodes fabricated from an electrically conductive boride or boron-doped material can be utilized as an efficient source of boron vapor. The process may optionally include a selection of an ambient gas species and its ambient pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

6) Resistive evaporation:

The boride material has been pressed, sintered, crystallized, and plasma sprayed, as methods to create filaments and electrodes. Any of these methods may be employed to make resistance evaporation sources. Direct electrical heating is defined here to encompass the class of evaporative coating processes that utilize the resistive passage of electricity through an electrically conductive material in order to heat and vaporize the material in order to transfer individual atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. An electrode fabricated from an electrically conductive boride or boron-doped material can be utilized as an efficient source of boron vapor. The process may optionally include a selection of an ambient gas species and its ambient

pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

7) Photon- or electron-induced evaporation:

Impingement of sufficiently energetic electrons or photons may easily be employed by traditional methods to create sufficient vapor for any of the instant applications. Photon-induced evaporation is defined here to encompass the class of evaporative coating processes that utilize photon-induced heating in order to heat and vaporize a material in order to transfer individual atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. Electron-induced evaporation is defined here to encompass the class of evaporative coating processes that utilize energetic electron beam-induced heating in order to heat and vaporize a material in order to transfer atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. An evaporative source fabricated from a boride or boron-doped material can be utilized as an efficient source of boron vapor. The process may optionally include a selection of an ambient gas species and its ambient pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

These deposition processes may also co-deposit other materials with the boron in order to further modify properties for enhanced materials. For example, boron carbide (B_4C) is also a poor electrical conductor because it is covalently bonded. It is normally deposited using chemical vapor deposition. The addition of boron carbide powder and optionally fullerene carbon powder to the metal boride powder in plasma spray can allow the deposition of a boron carbide-like coating onto materials.

All of these applications and deposition techniques depend on the existence of an electrically conductive metal boride that consists of and can be deposited as substantially pure boron.

Ultra-high boron atomic ratio materials have been demonstrated to produce substantially pure monoatomic boron and boron cluster vapor when sufficiently energized. Under proper growth conditions wherein temperature, pressure, atmosphere, and electromagnetic fields may be controlled, these vapors have been demonstrated to self-organize into various forms such as single and layered sheets, bundles of fibers, nanotubes of various kinds, spheres, and new crystalline forms such as B_{32} . These have been predicted to have desirable properties for applications in electronics, electro-optics, optics, nanofabrication, surface modification and alloying of metals and ceramics, and physio-chemical applications such as propulsion, energy storage, neutron attenuation, and alpha particle generation. Some of these materials have also demonstrated hydrophilic properties which are highly desirable for medical applications where a large neutron absorbing cross section is required.

00950518.042300

These boron vapors are extremely reactive, demonstrating properties not evidenced in vapors derived from traditional boron -halide, -hydride, -carbide, -sulfide, -nitride, or -metal compounds. Early experiments have shown remarkable potential in wide areas of physical chemistry. By changing the background gas from inert to reactive, byproducts have been observed and analyzed, indicating that it is reasonable to expect new families of compounds in the carbides, hydrides, nitrides, halides, sulfides, and metals. Because of the novel physical and chemical properties of these vapors, it has also been possible to induce bonding of materials, such as tantalum and graphite, at temperatures well below what might be expected to be the temperature of what in this case would be TaC. Materials as dissimilar as zirconium oxide and molybdenum have been observed to bond in similar circumstances. The precursor material, when in the mixed vapor state, has been observed to adhere readily to Al, Al₂O₃, C, Si, SiO₂, W, Ta, Mo, steel, WC, Cu, aerogel, etc. The mechanism is believed to be some combination of physio-chemical boundary layering effects such that the boron vapor reacts with both surfaces to create the bond, in effect acting as a glue. Given the dissimilarity of materials so far tested, and the potential reactivity of boron, this would seem to indicate that novel compounds could be predicted for all materials but the noble gases, which simply facilitate the creation of new boron forms, which may each themselves have unique properties.

Alternatively, carbon fullerene vapors are combined with the above-mentioned boron vapors to form novel cluster and nanotube related structures. It is also predicted, that in the presence of sulfur, these boron and boron-carbon structures will take on properties conducive to the filling of the open volumes of the cluster and nanotube structures with different structures, for example nanotubes filled with spheres or solid material. Such materials would be electrically

[illegible]

1. A method of creation of targets for sputtering, cathodic arc, electron beam, and laser ablation processing.

3. A method of depositing the material on a removeable form for the creation of freestanding parts demonstrating the above-mentioned properties.

Materials with boron ratios of 12 or greater may also be used for conductive coating
es where the metal component volatilizes before or congruent with the boron fraction.

BRIEF SUMMARY OF THE INVENTION

19

It is a further object of this invention to provide such a method for generating substantially pure boron such that the coating feedstock and the resultant coating are electrically conductive.

It is a further object of this invention to provide such a method for generating substantially pure boron such that extremely thick coatings can be obtained using well known coating technologies.

It is a further object of this invention to provide such a method for generating substantially pure boron such that the use of toxic chemicals may be avoided.

It is realized that the use of elemental boron as a feedstock in various well known coating technologies, such as cathodic arc, plasma spray, DC magnetron, electric arc, inductively heated evaporation, and electric current heated powder evaporation, does not perform reliably due to the lack of electrical conductivity and high thermal stability of elemental boron.

It is further realized that there exist metal boride compounds in which the companion metal represents less than 8 atomic percent of the compound.

It is further realized that said metal boride compounds are all electrically conductive.

It is further realized that when the companion metal does not readily vaporize, the metal remains present, permitting a gradual thermal decomposition through successive borides from a high boron-to-metal ratio towards the ratio of 4.

It is further realized that of the metal borides, only yttrium, holmium, erbium, thulium, terbium, gadolinium, and lutetium borides do not readily vaporize the metal component together with the boron.

008340 - BT50560

The phase diagram of yttrium and boron is shown in Figure 1. It shows that the higher boron-to-metal ratio borides decompose prior to melting. There exists a lower ratio boride that decomposes at a higher temperature in each case, thus indicating that there will be a successive loss of boron as a vapor with the next lower ratio boride as the decomposition product until YB_4 is reached. The phase diagram shows that YB_4 does not decompose in the solid state and is the most refractory of the several borides. Thus, it is the end product of the chain of decomposition. This interpretation of the phase diagram is confirmed experimentally by data presented in *The Handbook of High Temperature Compounds* (Kosalapova, 1990), pages 175-176, incorporated herein by reference. The table on these pages gives the measured vapor pressure of species resulting from thermal decomposition of most of the metal borides. It may be seen from the table that only yttrium, holmium, erbium, thulium, terbium, gadolinium, and lutetium borides decompose to only pure boron vapor instead of metal and boron vapor. It may also be seen that only the hexaborides and the higher atomic ratio borides of these metals decompose in this manner.

The log of the vapor pressure of boron is given in the table only at 1823°K (1550°C). When converted into millitorr units, the values for YB_6 , HoB_6 , and ErB_6 are 4.6, 34, and 56 millitorr. These values are typically quite temperature sensitive, increasing rapidly with greater temperature. These vapor pressure values are in the range suitable for use for physical vapor deposition and coatings.

The borides that have greater boron-to-metal ratios provide the greatest amount of boron vapor before the decomposition is halted at the tetraboride state. Thus, it is preferable to use

feedstock material that is as enriched as possible in the higher boron ratios and which has as little as possible of the lowest ratios, typically the diboride and tetraboride.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Other objects, features and advantages will occur to those skilled in the art from the following description of a preferred embodiment and the accompanying drawings in which:

FIG. 1 is a copy of the phase diagram of yttrium and boron taken from the ASM Metals Handbook, volume 1, page 556, incorporated herein by reference.

FIG. 2 is a copy of an EDAX measurement of the coating produced in EXAMPLE 5. The peak at the far left is due to boron coating. The other peaks are from the glass substrate.

EXAMPLE 1

YB₆₆ powder in the form of typically 50 to 75 micrometer particles has been used as the feedstock in an industrial plasma spray system utilizing argon gas as a carrier. The powder has been observed to spray easily and produce a characteristic granular deposit which can readily be built up to considerable thickness easily exceeding 3 mm. The deposit adheres readily to a wide variety of materials, including aluminum, steel, titanium, carbon, molybdenum, tungsten, tantalum, silicon, alumina, silica, zirconia, boron nitride, porcelain, and an aerogel foam. Good adhesion has been observed for all substrate materials tested. The resultant coating layer is extremely hard and difficult to break. In the case of a carbon substrate, for example, the graphite substrate will typically split or shatter prior to the debonding or failure of the coating. The

coating has been rapidly deposited over large surface areas and surfaces with complex shapes using well known plasma spray methods.

EXAMPLE 2

YB₆₆ has been plasma spray coated onto a tungsten coil filament for use as an electron emitter in an ion source. In addition, other ion source components, including the molybdenum arc chamber walls and graphite electron repeller, have been similarly coated in order to produce an ion source with enhanced boron emission as well as to minimize the output of contaminating atomic species. The tungsten coil filament has been heated to near its normal operating temperature when only the tungsten surface is exposed, and the filament has been observed to produce electrons capable of sustaining the arc discharge of the ion source. The coating was found to melt at the operating temperature of the filament, but the liquid coating did not alter the electron emission properties. The coated filament was found to enhance the boron output of the ion source, and the coating was not observed to detract from the normal filament lifetime, and tungsten contamination of the plasma was significantly diminished. If a boride is taken from the list in which the boron vaporizes preferentially before the metal, for example YB₆₆, then there is little or no metal component in the resultant ion beam according to a magnetic mass analysis of the beam.

EXAMPLE 3

A DC magnetron sputter target has been formed using buildup of a 1.5 mm thick coating of YB₆₆ using plasma spray. The sputter target transferred boron at a rate which was approximately 10 times greater than from RF sputtering. Sputter targets have been made by coating on a backing of graphite, copper and other materials.

EXAMPLE 4

A cathodic arc cathode has been formed in a few minutes by plasma spray of YB_{66} onto a graphite substrate. The coating was 3 mm thick. A cathodic arc system was operated with the said cathode at an arc current of nominally 50 Amperes in a background pressure of 10 millitorr of argon for 5 minutes. The output of the cathodic arc was directed towards a glass microscope slide target, and a grey, highly reflective boron-rich deposit was produced which was about 5 micrometers thick.

EXAMPLE 5

A high electric current of 75 Amperes has been drawn between two graphite electrodes connected by an excess of YB_{66} powder while in vacuum. The powder was observed to melt and begin emitting boron vapor, which could be used to coat a glass slide test sample. The thickness of powder separating the electrodes has been up to 2.5 cm, demonstrating the electrical conductivity of the boride. A high coating rate of over 0.003 inches per minute at a distance of 2 inches from the evaporation source was observed. FIG. 2 shows an EDAX analysis of the resultant coating material. EDAX is insensitive to light elements, such as boron, so the boron peak observed at the far left in the mass spectrum appears unnaturally small compared to the background elements from the glass slide substrate.

EXAMPLE 6

Nanostructures of boron have been fabricated in the form sheets, coiled nanotube-like tubular sheets, and wire-like filament structures. The structures have appeared following operation of a plasma chamber using a nitrogen + hydrogen mixture known as forming gas. The types of structures varied with collecting surface temperature, which was typically in the range of

800 to 1000 degrees centigrade. The materials were hydroscopic which could be reversed in vacuum. The observed structures could change form following this process.

Although specific features of the invention are shown in some drawings and not others, this is for convenience only and some features may be combined with any or all of the other features in accordance with the invention.

Other embodiments will occur to those skilled in the art and are within the following claims: